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VOL. 21, SEC. A. AUGUST, 1943 NUMBER 8

THE MAGNETO-OPTIC ROTATION OF HYDROGEN PEROXIDE[1]

BY PAUL A. GIGUÈRE[2] AND H. FEENY[3]

Abstract

The magnetic rotatory power of aqueous solutions of hydrogen peroxide of various concentrations was measured at 10° C. with the sodium *D*-line and the yellow, green, and blue lines of mercury. By extrapolation the Verdet constant of hydrogen peroxide for the sodium light was found to be 0.01148 ± 0.001 minute per gauss-cm., as compared with 0.01309 for water.

The purpose of the work described in this paper was to determine the Verdet constant of hydrogen peroxide about which no experimental data can be found in the literature. Although the magnetic rotatory power is somewhat related to the molecular structure, the present investigation could not be expected to add much to what is already known regarding the constitution of hydrogen peroxide.

The apparatus used consisted of a solenoid on to which were fitted the optical parts of a good polarimeter. The solenoid was made by winding 3386 turns of No. 14 enameled magnet wire on a copper tube 50 cm. long and 2.5 cm. in diameter. As the power dissipated in normal operation was about 1.5 kw. the solenoid was cooled by the following method. The winding was divided into 10 equal sections 5 cm. long and separated from one another by thin brass disks soldered to the central tube. To the periphery of these disks were soldered copper tubes through which tap water was circulated. Such a set-up could support a steady current of 12 amp., and even a 25 amp. current for short intervals without undue overheating. Only the central portion, 30 cm., of the solenoid was used, in order to obtain a uniform magnetic field. Over this length the calculated value of the field was found to agree to 1 part in 100 with that observed by measuring the Verdet constant of water. (The radius of the innermost layer of wire being 26 mm., and that of the outermost one, 69 mm., the calculated value of $\int H\,dl$ is 2430 gauss-cm. per amp.) The 20 amp. current normally used was supplied by storage batteries. It was controlled by one operator by means of a fine adjustment rheostat and it was read to ± 0.1 amp. on a Weston 30 amp. ammeter equipped with a mirror scale.

The polarizing and analysing Nicols were taken from a Schmidt and Haensch polarimeter of the "Lippich" half-shade type. The rotation of the

[1] *Manuscript received June 23, 1943.*
Contribution from the Department of Physics, Laval University, Quebec, Que.

[2] *Assistant Professor of Physical Chemistry.*

[3] *Assistant Professor of Physics.*

analyser could be read to within 0.01° by means of a vernier and telescope. Occasionally the setting of the half-shade had to be changed to suit the intensity and visibility of the various wave-lengths. The sodium light was obtained from an Osram lamp, and the mercury lines, from a Hanovia quartz arc. In the latter case a Hilger constant deviation spectroscope was used as a monochromator to separate the three lines, λ4358, 5461, and 5780. The cell containing the liquid to be investigated was made from a Pyrex tube 30 cm. long and 10 mm. in diameter. The ends were ground flat and polished and small Pyrex windows were sealed on by applying Apiezon *W* wax on the outer rim of the tube. Thus the hydrogen peroxide came in contact with nothing but glass and no trouble due to decomposition was experienced.

Because of lack of space no water jacket could be provided around the cell. Instead, the solution to be measured was cooled in an ice-bath before the cell was filled, and it was quickly slipped into the solenoid. The measurements were not started until the water had circulated long enough in the apparatus to bring it to constant temperature. The electric current was passed only for the short periods needed to make the readings. Unless these precautions were taken, difficulties were met on account of the slight variation in density and refractive index of the solutions. Blank runs made with a thermometer revealed that during one set of measurements the average temperature inside the apparatus remained at 10° ± 2° C. The limit of accuracy of the measurements, as well as the small temperature coefficient of the Faraday effect, did not warrant a better control.

The solutions of hydrogen peroxide were prepared by fractional distillation, under reduced pressure, of the 30% commercial product. They were analysed before and after the measurements by taking the refractive index (2). A trace of an inhibitor, sodium metaphosphate, was added to the more concentrated ones to prevent any decomposition.

Results

The apparatus was first calibrated with water after correcting for the windows of the cell. For each wave-length five readings were taken with the current on, then five zeros, and finally five more readings with the current reversed. Table I shows the values observed in this calibration with the sodium light. More readings were taken with the sodium light in order to obtain with as much accuracy as possible the Verdet conversion factor of the apparatus. As a rule the measurements were reproducible to the same accuracy as shown here except those with the blue line of mercury for which the deviations were two to four times as large. The fact, however, that in the latter measurements the rotation was double that for the sodium light partly compensated for this inaccuracy.

The results of the measurements are summed up in Table II along with data on the density (4) and the refractive index (2) of the solutions. When plotted in a graph, Fig. 1, the Verdet constant of the solutions is found to follow the mixture rule to within the accuracy of the measurements. By

TABLE I

CALIBRATION DATA

(For distilled water and the sodium light)

No.	θ_R	θ_0	θ_L	$\theta_L - \theta_0$	$\theta_0 - \theta_R$	$\frac{1}{2}(\theta_L - \theta_R)$	$\theta/_{\text{ampere}}$
1	353.68	4.51	15.39	10.88	10.83	10.86	0.543
2	353.68	4.52	15.34	10.82	10.84	10.83	0.542
3	353.64	4.53	15.43	10.90	10.89	10.89	0.545
4	353.66	4.51	15.41	10.90	10.85	10.88	0.544
5	353.63	4.50	15.40	10.90	10.87	10.89	0.544
6	353.61	4.50	15.41	10.91	10.89	10.90	0.545
7	353.62	4.47	15.41	10.94	10.85	10.89	0.545
8	353.59	4.49	15.45	10.96	10.90	10.93	0.546
9	353.65	4.47	15.42	10.95	10.82	10.89	0.545
10	353.64	4.50	15.38	10.88	10.86	10.87	0.543
						Mean:	0.544 ± 0.002

Correction for cell: 0.005° per amp.
Apparatus constant: 0.0243 Verdet unit per degree-amp.

TABLE II

EXPERIMENTAL RESULTS

H_2O_2, %	Mole fraction	Density, 20° C.	Refractive index, 20° C.	Verdet constant × 10^3			
				λ 5893	λ 5780	λ 5461	λ 4358
0.0	0.0	0.9982	1.3330	13.09	13.64	15.40	25.21
18.1	0.105	1.0648	1.3447	12.91	13.38	15.13	25.00
38.1	0.246	1.1456	1.3585	12.69	13.15	14.86	24.47
50.9	0.354	1.2005	1.3680	12.53	12.98	14.60	24.22
62.0	0.463	1.2488	1.3766	12.30	12.80	14.43	24.11
78.5	0.659	1.3314	1.3899	11.98	12.45	14.07	23.45
96.0	0.927	1.4230	1.4052	11.60	12.03	13.64	22.70

TABLE III

MAGNETO-OPTIC CONSTANTS OF HYDROGEN PEROXIDE

Constant		Found	Calc.
Verdet constant × 10^3 at 10° C.	λ 5893	11.48	—
Verdet constant × 10^3 at 10° C.	λ 5780	11.90	11.98
Verdet constant × 10^3 at 10° C.	λ 5461	13.52	13.59
Verdet constant × 10^3 at 10° C.	λ 4359	22.65	—
Refractive index, n_D			1.4112
Refractive index, $n_{\lambda 4359}$			1.4200
Rotation constant, C		869 891	
Rotation constant, K		−0.413 187	
Dispersion constant, λ_0		1 005.1	
Molecular magnetic rotation $[M]$		1.173	0.890

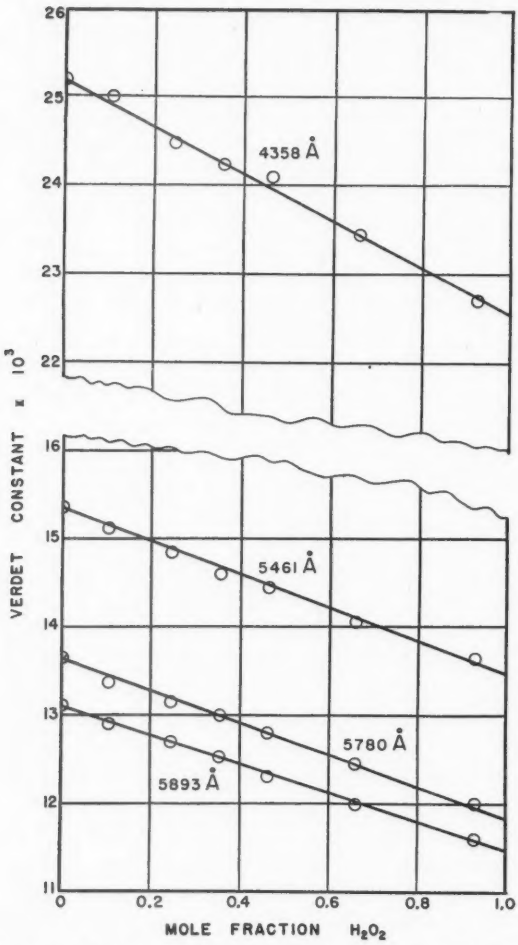

FIG. 1. *Magnetic rotatory power of aqueous solutions of hydrogen peroxide at 10° C.*

extrapolation of these curves the Verdet constants of pure hydrogen peroxide given in Table III were obtained. They are believed to be correct to within 1%. The dispersion constants for the magnetic rotation of hydrogen peroxide were calculated by means of Richardson's formula (1):

$$n\,\lambda^2\,V = C\left[K + \frac{\lambda^4}{(\lambda^2 - \lambda_0^2)^2}\right],$$

in which n is the refractive index, and V the Verdet constant of the liquid for the wave-length λ. At this point it may be mentioned that the observed value of the molecular magnetic rotation (3) of hydrogen peroxide is appreci-

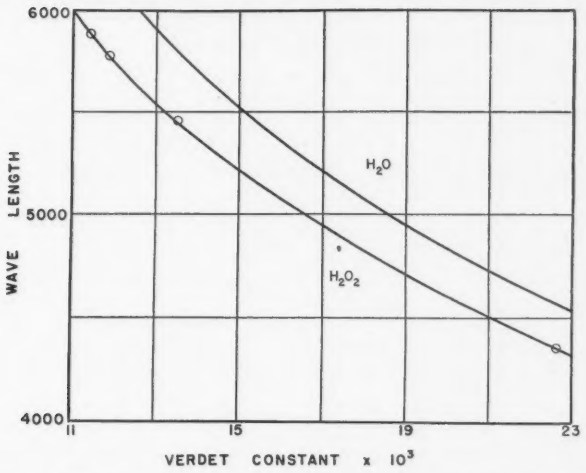

FIG. 2. *Dispersion of the magnetic rotation of hydrogen peroxide and water.*

ably higher than that calculated from the atomic equivalents of Perkins. A similar condition is noted in the values of the molecular refraction of this compound (2), and the same explanation can probably be given here—namely, that the molar magnetic rotation cannot be strictly additive for elements (such as oxygen) that possess lone pairs of electrons in the combined state.

Acknowledgment

The authors wish to express their appreciation to Prof. F. Rasetti for many helpful suggestions and his continued interest in this work.

References

1. DRUDE, P. The theory of optics. Longmans, Green, and Company, New York. 1933.
2. GIGUÈRE, P. A. Can. J. Research, B, 21 : 156-162. 1943.
3. GLASSTONE, S. Text-book of physical chemistry. D. Van Nostrand Company, Inc., New York. 1940.
4. MAASS, O. AND HATCHER, W. H. J. Am. Chem. Soc. 42 : 2548-2569. 1920.

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THE MERCURY PHOTOSENSITIZED DECOMPOSITION OF *n*-BUTANE[1]

BY A. W. HAY[2] AND C. A. WINKLER[3]

Abstract

The mercury photosensitized decomposition of *n*-butane at 100°, 175°, and 250° C. yields hydrogen, octanes, and dodecanes as the main products. The mechanism of the reaction is concluded to be a C—H bond split, followed by radical combination reactions.

Introduction

Valuable information concerning the kinetics of elementary processes has been obtained by the investigation of photosensitized reactions. With ethane (8, 13) and propane (9) the primary process appears to be

$$\begin{aligned} RH + Hg\ (^3P_1) &= R + HgH \\ &= R + Hg + H, \end{aligned}$$

where R is C_2H_5 or C_3H_7, followed by secondary reactions of the radicals to form the final products.

Little work is reported on the photosensitized reactions of *n*-butane. Taylor and Hill (13) found reaction to proceed more quickly in butane–hydrogen mixtures than in ethane–hydrogen or propane–hydrogen mixtures. Steacie and Phillips (11), in the course of another investigation, made one run with *n*-butane and obtained hydrogen and liquid products. In view of the interest attached to reactions of the aliphatic free radicals, it seemed desirable to extend the knowledge of the mercury photosensitized reactions of *n*-butane.

Experimental

The apparatus was similar in all essentials to that employed by Steacie and Dewar (9). Necessary modifications are indicated in Fig. 1. A mercury saturator *S* operated at 60° C. supplied the mercury vapour to saturate the gas, excess mercury at 20° C. being removed in trap *D*. Gas was circulated by the pump *P*, which consisted of a brass tube fitted with a piston, which was driven back and forth by an external solenoid sliding on the tube. The displacement of the pump was 312 ml. It was connected at *R* and *C* to a set of mercury valves so arranged that the gas always flowed so as to enter the reaction vessel through the saturator.

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[2] *Holder of a Studentship under the National Research Council of Canada.*

[3] *Assistant Professor of Chemistry.*

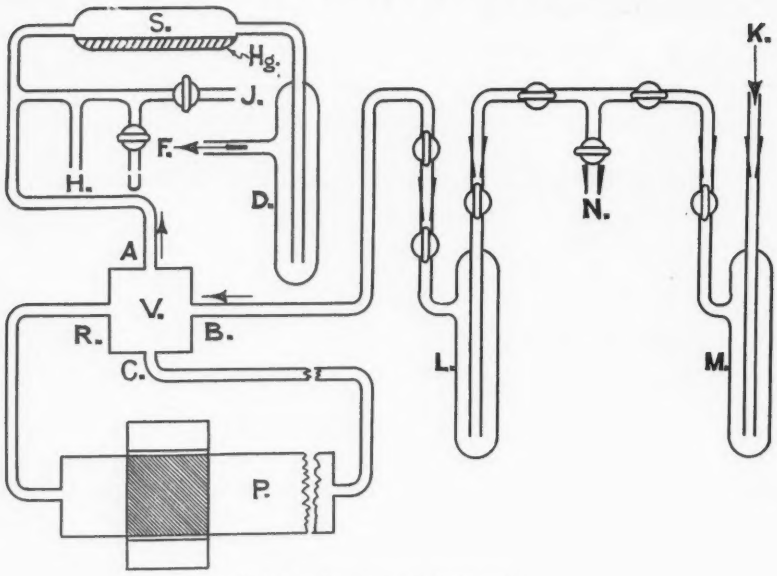

FIG. 1. *Arrangement of apparatus.*

A combined light source and reaction vessel, similar to that described by Steacie and Phillips (11), was employed. It was equipped with a gas inlet connected to *F* on trap *D*, and a gas outlet connected to *K* above trap *M*. A thermocouple well was provided for measuring the temperature of the reaction vessel, which, with the exception of the electrode chambers of the lamp, was enclosed in an electrically heated furnace. The volume of the vessel was 870 ml.

The condensable products of the reaction were collected in traps *M* and *L*, which were provided with ground joints so that they could be removed for weighing. In early runs at 100° C., the furnace was in a horizontal position, and the products were collected in trap *L* maintained at −40° C. However, on raising the oven temperature to 175° C., comparatively large amounts of liquid distilled out of the reaction vessel and condensed in the adjoining tubing. The work was repeated therefore with the reaction vessel and furnace in a vertical position directly above trap *M* maintained at 0° C.

The total volume of the main portion of the apparatus was 1780 ml. It was connected at *U* to a trap containing liquid butane, at *H* to a manometer, at *J* to a McLeod gauge, mercury diffusion pump, and Hyvac pump. A Toepler pump and gas holder were connected to the system at *N*.

It was shown by Steacie and Phillips (11) that the radiation from the type of lamp employed in this investigation is essentially composed of one wavelength, namely, the mercury line at 2537 Å. The intensity of this radiation

was determined by measuring the rate of hydrolysis of monochloracetic acid. Half-normal acid was illuminated at 35° C. for a definite period of time. Aliquot samples of the illuminated solution were then analysed by adding excess $N/2$ silver nitrate solution and back-titrating with potassium thiocyanate solution, using ferric alum as indicator. The mean of a number of measurements gave a value of 3.16×10^{-6} einsteins per sec. for the total resonance radiation entering the reaction vessel, based on Rudberg's value of one for the quantum yield (3). Although this value for the quantum yield is too low (5), it was used to facilitate comparison with other work.

All runs were carried out at the vapour pressure of butane at −40° C. (about 12.5 cm. of mercury), the period of illumination being generally five hours. The initial pressure of butane was taken with the traps L and M at 0° C.

Preliminary work indicated that the liquid products formed were octanes and dodecanes. Thus, by maintaining traps L and M at 0° C., for a short while at the end of a run, the pressure of the gaseous products and unused butane could be determined. Then, by keeping trap M at 0° C., and cooling trap L with liquid air, the gaseous products were circulated until the manometer gave concordant readings on stopping the pump. Thus, all possible gaseous products, with the exception of methane and hydrogen, were removed from the system, and the pressure of hydrogen and methane (if present) could be determined. Trap L in liquid air was then removed from the system and liquid air placed around trap M. The furnace temperature was then raised to ensure trapping out all high boiling products that might have condensed on the wall of the reaction vessel. The hydrogen–methane fraction was removed with a Toepler pump into a gas holder, distilled through a Podbielniak type column to remove traces of higher hydrocarbons, and analysed by combustion. The contents of trap L were analysed by fractionation in the low temperature distillation unit, followed by combustion of the fractions. The high boiling fraction remaining in this trap after fractionation and the liquid collected in trap M were weighed and fractionated in a semi-micro distillation unit. Owing to the small amount of liquid produced, the products from a series of runs at a particular temperature were combined for this purpose. Tests for unsaturates were made from time to time by the usual absorption method.

The butane used was obtained from the Ohio Chemical Company. Although it contained no impurities detectable by the analytical methods employed, it was fractionated once before being admitted to the apparatus.

Experimental Results

The results obtained for the mercury photosensitized decomposition of *n*-butane at 100°, 175°, and 250° C. are given in Table I. The quantum yield given is based on the hydrogen produced, and may represent the over-all value for several reactions rather than that for butane decomposition alone.

TABLE I

RATE AND ANALYTICAL DATA FOR THE PHOTOSENSITIZED DECOMPOSITION OF *n*-BUTANE

Volume of system, 1780 ml. Butane vapour pressure, 12.5 cm.
Volume of reaction vessel, 870 ml. Trap temperature, −40° C.
Arc current, 89 ma. Circulating rate, 2.67 litres/min.
Resonance radiation absorbed, 3.16×10^{-6} einsteins/sec.

Temp., °C.	Decomposition rate, moles $\times 10^6$ per sec.	Over-all quantum yield of H_2	Products, moles $\times 10^2$			
			H_2	CH_4	C_8H_{18}	$C_{12}H_{26}$
100	0.764	0.19	1.06	—	0.359	0.529
100	0.825	0.19	1.11	—	0.351	0.518
99	0.787	0.19	1.09	—	0.342	0.500
175	1.28	0.25	1.44	—	0.386	0.641
174	1.31	0.26	1.46	—	0.394	0.653
250	2.03	0.29	1.65	0.01	0.939	0.737
249	2.06	0.28	1.61	0.01	0.951	0.741
*249	5.81	0.29	1.89	0.04	1.01	0.694
*250	6.08	0.30	1.90	0.04	1.01	0.759

** A new lamp with an intensity of 7.33×10^{-6} einsteins per sec. was used in these runs.*

The liquid condensate is expressed as C_8H_{18} and $C_{12}H_{26}$ since boiling point determinations indicated octanes and dodecanes to be the main components.

The results of the condensate analyses are given in Table II. The boiling points of the "light" fractions obtained at all temperatures studied are definitely in the boiling range of the octanes, while the boiling point of the "heavy" fraction from the runs at 100° C. is definitely in the dodecane boiling range. In the absence of methane, ethane, and propane the "heavy" products of the runs at 175° C. boiling within the dodecane range are probably also

TABLE II

LIQUID CONDENSATE ANALYSIS

Temp., °C.		Boiling points, °C.	Weight %	Remarks
100	Fraction 1	115.5	31.6	Octanes
	Fraction 2	195 – 200	68.4	Dodecanes
175	Fraction 1	115.5	28.7	Octanes
	Fraction 2	160	71.3	Dodecanes
250	Fraction 1	109	46.2	Octanes and lower
	Fraction 2	160	53.8	Dodecanes and lower
250	Fraction 1	110	49.2	Octanes and lower
	Fraction 2	160	50.8	Dodecanes and lower

dodecanes. In the runs at 250° C. the formation of appreciable quantities of methane does not preclude the presence of small amounts of pentanes, heptanes, nonanes, and undecanes. However, from the boiling points, and the nature of the gaseous products, it appears that isomers of normal octane and dodecane are the main liquid products formed.

Discussion

The fact that the main products of the mercury photosensitized decomposition of *n*-butane are hydrogen, octanes, and dodecanes at all temperatures studied indicates the primary step to be production of butyl radicals, followed by their recombination, thus:

$$C_4H_{10} + Hg(^3P_1) = C_4H_9 + Hg(^1S_0) + H$$

or possibly

$$C_4H_{10} + Hg(^3P_1) = C_4H_9 + HgH$$
$$= C_4H_9 + Hg + H$$

followed by

$$2\,C_4H_9 = C_8H_{18}$$

The high butane pressure in the system should favour removal of the hydrogen atoms formed in the primary step by the reaction

$$H + C_4H_{10} \longrightarrow C_4H_9 + H_2\,,$$

which then would constitute an important source of butyl radicals (10). As hydrogen accumulates during a run, an increasing proportion of butyl radicals will be derived from such an atom reaction, as a result of hydrogen atom production by photosensitized decomposition of hydrogen molecules.

Reaction between a butyl radical and a butane molecule to form octane, with elimination of a hydrogen atom, cannot be considered as a source of octanes, since this type of reaction is estimated to have a high activation energy (10).

The formation of dodecanes indicates that octyl radicals are produced from the octane present, in the same manner as butyl radicals are produced from butane, and that butyl radicals and octyl radicals then combine to form dodecane. Reaction between butyl radicals and octane molecules to form dodecane and hydrogen atoms must be ruled out on the same grounds as the corresponding reaction between butyl radicals and butane mentioned previously. However, the preponderance of dodecanes over octanes in the runs at 100° C. and 175° C. suggests the formation of octyl radicals at these temperatures by the reaction

$$C_4H_9 + C_8H_{18} = C_4H_{10} + C_8H_{17}\,.$$

This reaction is of the same type as

$$CH_3 + C_4H_{10} = CH_4 + C_4H_9\,,$$

which is known to occur at these temperatures (4).

The reversal of the octane–dodecane ratio at 250° C. is probably due to decomposition of octyl by

$$C_8H_{17} = C_4H_9 + C_4H_8$$

followed by

$$H + C_4H_8 = C_4H_9 .$$

This suggestion is in agreement with the fact that no considerable amounts of methane, ethane, and propane, nor of liquids boiling in other than the octane and dodecane ranges, were found in the products. The lack of unsaturates in both the liquid and gaseous products indicates that any butylene formed is hydrogenated by the hydrogen atoms present.

The mechanism of the *n*-butane decomposition is similar, in certain respects at least, to that of the mercury photosensitized decomposition of propane (9). The main reactions in the propane decomposition were postulated to be:

$$\begin{aligned} C_3H_8 + Hg(^3P_1) &= C_3H_7 + H + Hg(^1S_0) \\ H_2 + Hg(^3P_1) &= 2\,H + Hg(^1S_0) \\ H + C_3H_8 &= C_3H_7 + H_2 \\ 2\,C_3H_7 &= C_6H_{14} \\ 2\,H &= H_2 \\ C_3H_7 + C_3H_8 &= C_6H_{14} + H \end{aligned}$$

With both propane and butane, the primary act apparently involves removal of a hydrogen atom, followed by radical recombination. However, only small amounts of hydrocarbons boiling higher than hexane are produced in the propane reaction, whereas the formation of higher boiling products is one of the main characteristics of the decomposition of *n*-butane. It is hoped that results obtained in a study of the photosensitized decomposition of isobutane (1) will provide an explanation of the differences in type of the heavier products resulting from the photosensitized decompositions of the lower hydrocarbons.

The results of the present study are in no way incompatible with those found for the reaction of *n*-butane with hydrogen atoms (7, 15), where methane and ethane were the main products. The preponderance of lower hydrocarbons in the hydrogen atom reaction was explained on the basis of progressive decomposition of radicals by reaction with hydrogen atoms. In the photosensitized reaction, the low hydrogen atom and butyl radical concentrations, relative to the high butane pressure, will favour radical recombination, rather than radical decomposition reactions.

It is not possible, without much more detailed analytical data than those available to determine whether a primary or secondary hydrogen atom is removed from the molecule in the primary step of the photosensitized decomposition of *n*-butane. Perhaps both processes are involved. However, it appears that with propane the removal of a secondary hydrogen atom is favoured (9), and it seems probable that the same should be true for the *n*-butane reaction. Certainly, the observed boiling points of the octane fractions would not be opposed to such a conclusion (cf. Reference (2)).

References

1. DARWENT, B. DE B. and WINKLER, C. A. Unpublished results.
2. EGLOFF, G. Physical constants of hydrocarbons, Vol. I. Reinhold Publishing Corporation, New York. 1939.
3. RUDBERG, E. Z. Physik, 24 : 247-263. 1924.
4. SMITH, J. O., Jr. and TAYLOR, H. S. J. Chem. Phys. 7 : 390-396. 1939.
5. SMITH, R. N., LEIGHTON, P. A., and LEIGHTON, W. G. J. Am. Chem. Soc. 61 : 2299-2301. 1939.
6. STEACIE, E. W. R., ALEXANDER, W. A., and PHILLIPS, N. W. F. Can. J. Research, B, 16 : 314-318. 1938.
7. STEACIE, E. W. R. and BROWN, E. A. J. Chem. Phys. 8 : 734-738. 1940.
8. STEACIE, E. W. R. and CUNNINGHAM, R. L. J. Chem. Phys. 8 : 800-804. 1940.
9. STEACIE, E. W. R. and DEWAR, D. J. J. Chem. Phys. 8 : 571-576. 1940.
10. STEACIE, E. W. R., LEROY, D. J., and POTVIN, R. J. Chem. Phys. 9 : 306-314. 1941.
11. STEACIE, E. W. R. and PHILLIPS, N. W. F. J. Chem. Phys. 4 : 461-468. 1936.
12. STEACIE, E. W. R. and PHILLIPS, N. W. F. Can. J. Research, B, 16 : 303-313. 1938.
13. TAYLOR, H. S. and HILL, D. G. Z. physik. Chem. B, 2 : 449-450. 1929.
14. TAYLOR, H. S. and HILL, D. G. J. Am. Chem. Soc. 51 : 2922-2936. 1929.
15. TRENNER, N. R., MORIKAWA, K., and TAYLOR, H. S. J. Chem. Phys. 5 : 203-211. 1937.

THE REFRACTIVE INDICES OF HYDROGEN PEROXIDE AND ITS AQUEOUS SOLUTIONS[1]

By Paul A. Giguère[2]

Abstract

The refractive indices of aqueous solutions of hydrogen peroxide for the *C*-, *F*-, and *G*-lines of hydrogen and the sodium *D*-line have been measured over the whole range of concentration at four temperatures: 16°, 20°, 24°, and 28° C. The results obtained with the hydrogen lines are somewhat different from those of Cuthbertson and Maass. A possible explanation of this discrepancy is given. By extrapolation it was found that for pure hydrogen peroxide $n_D = 1.4087$ at 20°, a value in good agreement with previous determinations. The refractive index affords a rapid and fairly accurate method for determining the concentration of solutions of hydrogen peroxide.

In the course of research work carried out in these laboratories, a great number of analyses had to be made in order to determine the concentration of aqueous solutions of hydrogen peroxide. Since two components only were involved it was believed worth while to investigate the feasibility of replacing the tedious titrations with potassium permanganate by some physical measurement, such as the density or the refractive index. The densities of hydrogen peroxide and of its solutions have been measured accurately by Maass and Hatcher (7) at various temperatures. This property was found to vary regularly with concentration from the value for water to that for the pure peroxide, 1.4418 at 20°. However the usual methods for determining the density of liquids are either too complicated or not accurate enough to offer any advantage in the present case. This determination is further handicapped by the tendency of hydrogen peroxide to decompose spontaneously.

The refractive index, on the other hand, provides a much more adequate method of analysis, at least if the proper type of instrument is used. Brühl (1) was the first to measure the refractive index of concentrated hydrogen peroxide. As the exact composition of his solutions was not known his results were of little use. Later Maass and Hatcher (7) repeated these measurements for pure hydrogen peroxide and for a concentrated solution by the goniometer method. Their results are shown in Table I. Cuthbertson and Maass (3) extended these measurements to cover the entire concentration range and for the three hydrogen lines. Thus they found that the refractive index increases uniformly with concentration from that of water, $n_C = 1.3307$, to that of hydrogen peroxide, $n_C = 1.4050$ at 24.5°. As the refractivity of a solution can easily be determined to within 0.0001, the percentage of hydrogen peroxide could be known to within 0.14, which is sufficient for most purposes. Yet a trial determination, made with the data of Cuthbertson and Maass, gave

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Contribution from the Department of Chemistry, Laval University, Quebec, Que.
[2] *Assistant Professor of Physical Chemistry.*

results quite different from those of the chemical analysis and no better agreement could be reached subsequently in spite of a careful check. So it was decided to redetermine the refractive indices of a number of solutions and to include the *D*-line of sodium, which is the most commonly used.

Experimental

The measurements were made with a Pulfrich refractometer, the most convenient type in the case of corrosive and unstable liquids. Obviously enough an Abbé refractometer could not be used on account of the rapid decomposition of the peroxide on the etched surface of the prisms. With the Pulfrich instrument, only a very slight decomposition was observed on the rough portion of the prism, and this introduced no appreciable error. For the same reason the internal heater, made of metal, was never lowered into the cell. Instead, it was merely used as a cover for the cup, an important precaution in the case of solutions, as will be shown later. The temperature was kept constant to $\pm 0.2°$ by circulating water from a thermostat. The sources of light were a General Electric Sodium Lab-Arc and a long discharge tube for the hydrogen lines.

TABLE I

REFRACTIVE INDEX OF HYDROGEN PEROXIDE

H_2O_2, %	t, °C.	n_C	n_D	n_F	n_G	Author
99(?)	14.0	1.39839	1.40051	1.40514	1.40880	Brühl
99(?)	18.7		1.40650			Brühl
99(?)	19.6	1.40485	1.40695	1.41177	1.41561	Brühl
99(?)	20.4	1.40421	1.40624	1.41100	1.41494	Brühl
96.8	24		1.4043			Maass and Hatcher
99.9	22		1.4063*			Maass and Hatcher
100.0	16.0	1.4076	1.4097	1.4148	1.4186	This work
100.0	20.0	1.4066	1.4087	1.4136	1.4175	This work
100.0	24.0	1.4054	1.4076	1.4122	1.4160	This work
100.0	28.0	1.4040	1.4061	1.4111	1.4149	This work

* *As corrected by Cuthbertson and Maass.*

Throughout the measurements the following procedure was adopted: The solutions were prepared by mixing accurately weighed quantities of redistilled water and a concentrated solution of hydrogen peroxide made by fractional distillation of the 30% commercial product. The instrument was then checked by taking the refractive index of water. The values observed always agreed to the limit of accuracy with those given in the literature. After rinsing thoroughly with the solution to be analysed, the cell was filled, and the measurements made once the temperature equilibrium had been attained. Three or more readings were taken for each wave-length. The dispersion was also recorded in every case and the great number of data thus obtained helped in checking any possible error. Finally the solution was analysed by titration with standard permanganate.

Discussion of Results

The experimental results are given in Table II. These data were plotted on a large graph and extrapolated to 100% concentration to obtain the values for pure hydrogen peroxide shown in Table I. All the points fell closely on simple curves and no great deviation was observed even for the blue line of hydrogen, which is the most difficult to read. For convenience in analysing aqueous solutions of hydrogen peroxide the refractive index for the *D*-line of sodium at 20° for every concentration in steps of 0.2% is given in Table III, and the temperature correction for the same, in Table IV. The latter shows a temperature factor of 0.0003 per degree for the refractivity of hydrogen peroxide which is about three times that of water.

TABLE II

EXPERIMENTAL RESULTS

H_2O_2, %	0.0	10.0	19.8	30.8	41.1	49.7	60.0	70.1	79.9	90.4	99.0
At 16°											
n_C	1.3313	1.3380	1.3446	1.3522	1.3597	1.3659	1.3738	1.3820	1.3901	1.3991	1.4067
n_D	1.3333	1.3398	1.3465	1.3541	1.3616	1.3679	1.3759	1.3840	1.3922	1.4012	1.4089
n_F	1.3374	1.3440	1.3507	1.3585	1.3660	1.3723	1.3804	1.3886	1.3968	1.4058	1.4137
n_G	1.3405	1.3473	1.3540	1.3619	1.3695	1.3758	1.3842	1.3924	1.4007	1.4095	1.4176
At 20°											
n_C	1.3311	1.3375	1.3441	1.3515	1.3587	1.3651	1.3729	1.3811	1.3892	1.3980	1.4057
n_D	1.3329	1.3394	1.3460	1.3534	1.3607	1.3671	1.3749	1.3831	1.3912	1.4001	1.4079
n_F	1.3371	1.3435	1.3502	1.3577	1.3651	1.3715	1.3793	1.3876	1.3958	1.4047	1.4127
n_G	1.3402	1.3468	1.3536	1.3612	1.3685	1.3750	1.3830	1.3914	1.3995	1.4085	1.4167
At 24°											
n_C	1.3307	1.3370	1.3434	1.3508	1.3581	1.3643	1.3722	1.3804	1.3883	1.3969	1.4046
n_D	1.3326	1.3389	1.3453	1.3527	1.3601	1.3664	1.3743	1.3824	1.3903	1.3991	1.4067
n_F	1.3367	1.3431	1.3495	1.3569	1.3643	1.3707	1.3788	1.3870	1.3949	1.4037	1.4114
n_G	1.3400	1.3464	1.3529	1.3603	1.3678	1.3743	1.3822	1.3907	1.3985	1.4076	1.4153
At 28°											
n_C	1.3305	1.3365	1.3427	1.3499	1.3572	1.3636	1.3711	1.3796	1.3873	1.3959	1.4032
n_D	1.3322	1.3383	1.3446	1.3518	1.3592	1.3656	1.3731	1.3816	1.3893	1.3980	1.4053
n_F	1.3364	1.3424	1.3487	1.3561	1.3635	1.3700	1.3776	1.3861	1.3939	1.4027	1.4101
n_G	1.3396	1.3458	1.3522	1.3596	1.3669	1.3735	1.3812	1.3898	1.3976	1.4064	1.4140

As can be seen from Fig. 1, there is an appreciable discrepancy between the results of the present investigation at 24° and those of Cuthbertson and Maass. For instance they found $n_C = 1.3557$ for a 35.5% solution, whereas it should be 1.3539 to fit the curve presented here. Around 90% concentration, however, the two sets of measurements agree fairly well. This fact suggests the following explanation: Hydrogen peroxide is less volatile than water, and vapour pressure measurements have shown that its partial pressure

TABLE III

REFRACTIVE INDEX OF AQUEOUS SOLUTIONS OF HYDROGEN PEROXIDE AT 20° C. FOR THE SODIUM *D*-LINE

H_2O_2, %	0.0	0.2	0.4	0.6	0.8	H_2O_2, %	0.0	0.2	0.4	0.6	0.8
0	1.3 330	331	332	333	334	50	1.3 673	674	676	678	679
1	336	337	338	339	341	51	681	682	684	685	687
2	342	343	345	346	347	52	689	690	691	693	694
3	348	350	351	353	354	53	696	697	699	700	702
4	355	356	357	359	360	54	704	705	706	708	709
5	361	363	364	365	367	55	711	713	714	716	718
6	368	369	371	372	373	56	719	720	722	724	725
7	374	376	377	378	380	57	726	728	729	731	733
8	381	382	384	385	386	58	734	736	737	739	740
9	387	389	390	391	392	59	742	744	745	746	748
10	394	395	397	398	400	60	749	751	753	754	756
11	401	402	403	404	406	61	758	759	761	763	764
12	407	409	410	411	412	62	766	767	769	770	772
13	414	415	416	417	419	63	774	775	777	779	780
14	420	421	423	424	425	64	782	783	785	787	788
15	427	428	429	431	432	65	790	791	793	794	796
16	433	435	436	437	439	66	798	799	801	803	804
17	440	441	443	444	445	67	806	807	809	810	812
18	447	448	449	451	452	68	814	815	817	818	820
19	453	455	456	457	459	69	822	824	825	827	828
20	460	462	463	464	465	70	830	831	833	834	836
21	467	468	470	471	472	71	838	839	841	843	844
22	474	475	476	478	479	72	846	847	849	851	852
23	480	482	483	484	486	73	854	856	858	859	861
24	487	488	490	492	493	74	862	864	866	868	869
25	494	495	497	498	499	75	871	872	874	876	877
26	501	502	504	505	506	76	879	880	882	884	886
27	508	509	511	512	513	77	887	889	890	892	894
28	515	516	517	519	520	78	896	897	899	900	902
29	522	523	524	526	527	79	904	906	907	909	910
30	529	530	531	533	534	80	912	914	916	917	919
31	535	537	538	540	541	81	921	923	924	926	928
32	543	544	546	547	548	82	929	931	933	934	936
33	549	551	552	554	555	83	938	939	941	943	945
34	556	557	559	561	562	84	946	948	950	951	953
35	564	565	567	568	569	85	955	956	958	960	962
36	570	572	573	575	576	86	963	965	967	968	970
37	578	579	581	582	584	87	972	974	976	977	979
38	585	586	588	589	591	88	980	982	984	986	988
39	592	594	595	596	598	89	989	991	993	995	996
40	599	601	602	604	605	90	998	*000	*001	*003	*005
41	607	608	610	611	612	91	1.4 007	009	010	012	014
42	614	615	617	619	620	92	016	018	020	022	023
43	621	623	624	626	627	93	025	026	028	030	032
44	629	630	632	633	635	94	034	036	038	040	042
45	636	637	639	640	642	95	043	045	047	049	050
46	643	645	646	648	649	96	052	054	056	058	059
47	651	652	654	655	656	97	061	063	065	067	068
48	658	659	661	663	664	98	070	072	074	076	077
49	666	667	669	670	671	99	079	081	083	085	086

is lower than that of water over dilute solutions, and up to 90% (5). Such solutions will therefore become more concentrated on evaporating. Actually a test was made, in which the refractive index of a 30% solution was observed to change from 1.3514 to 1.3522 on standing only five minutes in the un-

TABLE IV

TEMPERATURE CORRECTIONS

Above 20° C. correction is added to, and below 20°, substracted from, the percentage of hydrogen peroxide (in Table III)

Temp., °C.	Approximate concentration								
	10	20	30	40	50	60	70	80	90
16	0.70	1.00	1.10	1.20	1.30	1.20	1.20	1.10	1.00
17	0.55	0.75	0.85	0.90	0.95	0.90	0.90	0.85	0.75
18	0.35	0.50	0.55	0.60	0.65	0.60	0.60	0.55	0.50
19	0.20	0.25	0.30	0.30	0.30	0.30	0.30	0.30	0.25
21	0.20	0.20	0.25	0.25	0.30	0.30	0.30	0.30	0.30
22	0.40	0.45	0.50	0.55	0.55	0.55	0.55	0.55	0.55
23	0.60	0.65	0.75	0.75	0.80	0.80	0.80	0.80	0.80
24	0.80	0.90	1.00	1.00	1.10	1.10	1.10	1.10	1.10
25	0.95	1.10	1.30	1.45	1.30	1.20	1.25	1.40	1.60
26	1.10	1.35	1.55	1.75	1.65	1.40	1.60	1.65	1.95
27	1.30	1.60	1.85	2.00	1.85	1.65	1.75	1.95	2.30
28	1.50	1.80	2.10	2.30	2.10	1.90	2.00	2.20	2.60

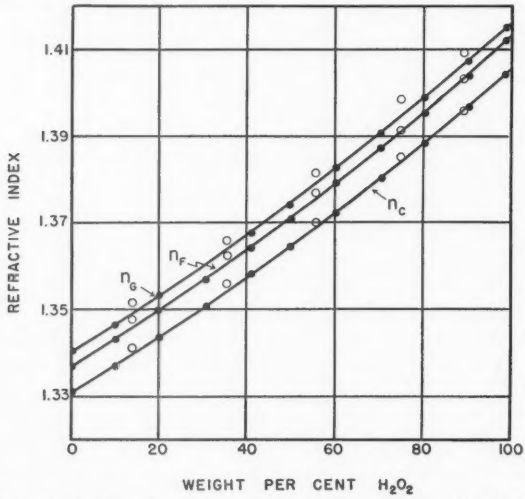

FIG. 1. *Refractive indices of aqueous solutions of hydrogen peroxide at 24° C. The white circles represent the results of Cuthbertson and Maass at 24.5°. There is no direct relation between the accuracy of the measurements and the radius of the circles or the thickness of the lines.*

covered cell on the Pulfrich refractometer. The importance of this factor has been discussed previously (2).

The various secondary constants given in Table V were derived from the refraction data of hydrogen peroxide. The corresponding values for water

are also shown for comparison (4). The specific refraction was calculated by means of the Lorenz–Lorentz formula. As has been pointed out previously, the observed value of the molecular refraction of hydrogen peroxide is larger than the sum of the refractive equivalents (Eisenlohr) for two hydroxyl oxygens and two hydrogen atoms, viz.: 5.25. This so-called exaltation was then interpreted in favour of an "unsaturated" formula, either with the two hydrogens attached to the same oxygen (3) or with multiple bonds between the two hydroxyl groups (10). Since the molecular structure of hydrogen peroxide is now well established, this constant is better explained in terms of electron groups instead of atomic equivalents (9). Thus the difference between the molecular refraction of hydrogen peroxide and that of water can be ascribed to the Ö–Ö electron group. Very nearly the same difference (2.2) exists between the lower alkyl peroxides and the corresponding ethers (8).

The polarizability and the average molecular radius were calculated from the well known equation (6):

$$\alpha = r^3 = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} \cdot \frac{3}{4\pi N}$$

from the data for the *D*-line at 20°. The results obtained for the dispersion in this investigation agree closely with those of Brühl.

TABLE V

CONSTANTS DERIVED FROM REFRACTION DATA

	Hydrogen peroxide	Water
Specific refraction, r_D	0.1713	0.2064
Molecular refraction, $[M]_D$	5.826	3.715
Polarizability, $\alpha \times 10^{24}$	2.31	1.48
Molecular radius, in Å	1.32	1.14
Molecular dispersion, $[M]_G - [M]_C$	1.3576	0.9285
Dispersion constant, $a \times 10^{-8}$	9.5729	7.4685
Characteristic frequency, $\nu_0 \times 10^{-4}$	10.0075	9.9516

The experimental results for the red and the blue lines of hydrogen at 20° C. were fitted into the simplified dispersion formula of Sellmeier:

$$n^2 - 1 = \frac{a}{\nu_0^2 - \nu^2}$$

and the two constants calculated. As a practical application, the refractive index provides a very convenient method for determining the composition of aqueous solutions of hydrogen peroxide. It is much more rapid than the volumetric analysis, although not so accurate, specially for the more dilute solutions. The influence of impurities can be neglected for all practical purposes.

References

1. BRÜHL, J. W. Ber. 28 : 2847-2866. 1895.
2. CHÉNEVEAU, C. Ann. chim. phys. (Sér. 8) 12 : 145-228, 289-393. 1907.
3. CUTHBERTSON, A. C. and MAASS, O. J. Am. Chem. Soc. 52 : 489-499. 1930.
4. DORSEY, N. E. Properties of ordinary water-substance. Reinhold Publishing Corporation, New York. 1940.
5. GIGUÈRE, P. A. AND MAASS, O. Can. J. Research, B, 18 : 181-193. 1940.
6. GLASSTONE, S. Text-book of physical chemistry. D. Van Nostrand Company, Inc. New York. 1940.
7. MAASS, O. and HATCHER, W. H. J. Am. Chem. Soc. 42 : 2548-2569. 1920.
8. RIECHE, A. Ber. B, 62 : 218-225. 1929.
9. SMYTH, C. P. Dielectric constants and molecular structure. The Chemical Catalog Company, Inc., New York. 1931.
10. STRECKER, W. and SPITALER, R. Ber. B, 59 : 1754-1775. 1926.

THE SYSTEM: SILVER-NITRATE–WATER[1]

By A. N. Campbell[2] and Mary L. Boyd[3]

Abstract

The temperature–concentration diagram has been determined for the system: silver-nitrate–water, from 0 to 100% silver nitrate, with greater accuracy than has previously been attained (especially with regard to thermostatic control and method of analysis). The equilibrium curve exhibits a eutectic point at −7.57° C. and 46.9% silver nitrate and also a break at about 159° where solid silver nitrate passes from the rhombic to the rhombohedral form.

The system silver-nitrate–water is of particular theoretical interest because it is one whose solubility curve extends to the melting point of the salt (7, pp. 163, 164). In most systems, this temperature is above the critical temperature of water and the solubility curve undergoes a rapid change of direction below the melting point of the salt. Although the general form of the curve is well known, the literature revealed very poor agreement among existing determinations, and, in general, there are few determinations of solubility above 100°, because of the experimental difficulties involved. The aim of this investigation was to determine by superior methods the temperature–concentration diagram under the vapour pressure of the system.

The ice curve has been determined by Rüdorff (17), Guthrie (9), Raoult (15), Arrhenius (1), and Roth (16).

The solubility curve has been determined by the following authors, over the range indicated; Kremers (12), 0 to 110°; Tilden and Shenstone (21), 125 to 133°; Etard (6), −7 to 182°; Schreinemakers (18), 30°; Bailey (2), 10–35°; Benrath *et al.* (3), 112–198° C.

Middelberg (13) found the eutectic temperature to be −7.3° at a concentration of 47.1% silver nitrate. Schreinemakers and de Baat (19) also give these values for the eutectic point, but this seems to be a mere quotation from Middelberg.

From measurements other than solubility it is known that silver nitrate exists in two crystalline forms, the temperature of transition being about 160° C. Below this temperature the crystalline form is rhombic and above it, hexagonal–rhombohedric. Hence, there should be a break in the solubility curve at this temperature, but it has not hitherto been observed, presumably because the measurements lacked the requisite accuracy.

The transition temperature has been determined by the following authors: Schwarz (20), 159.2–159.7° C.; Hissink (10), 159.8°; Zawidzki (23), 159.6°; Guinchant (8), 159°; Jänecke (11), 151–171°, 136–144°; Bridgman (4), 159.4°.

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[2] *Associate Professor of Chemistry.*

[3] *Graduate Student, 1942–43. Holder of a Bursary under the National Research Council of Canada.*

The most recent figures for the melting point of pure silver nitrate are those of Hissink (10) (208.6° C.), van Eyk (22) (208.5°), and Zawidzki (23) (208.6°).

Discussion of Existing Data

All the determinations of the ice curve are in fairly good agreement, with the exception of those of Guthrie (9). The graph of his data lies about 1° above that of the others or, in other words, his concentration values differ by 3 to 5% from those of others. The figures of Arrhenius (1) are of little value in this connection because his three points all refer to very dilute solutions. The determinations of Roth (16) are the most accurate since he alone analysed the equilibrium liquid, but here, too, the results are of little value to this investigation because he dealt with extremely dilute solutions. Raoult's figures (15) are the most valuable because his measurements were carried up to a concentration of 40% silver nitrate.

The numerous determinations of solubility, on the other hand, are in very poor agreement. In most of the investigations, there appears to have been no method of thermostatic control. Tilden and Shenstone (21) alone mention it: they were able to keep the temperature constant to within $\pm 2°$. The most complete data are those of Etard (6). He makes no mention of the fact that the solubility curve should exhibit a break at the transition temperature; Hissink (10) was the first to draw attention to this and to point out that Etard's theory—that the solubility curve was a straight line—must necessarily be incorrect. The method used by Benrath (3), which consists in placing known quantities of salt and water in sealed glass tubes and determining the temperature at which the last trace of solid disappears, is not susceptible of high accuracy and has the additional disadvantage that it is subjective.

The transition point and the melting point are known with a high degree of certainty. The heat effect and the volume change at the transition point are very small, and this will account for the difficulty of detecting this point as a break on the solubility curve. In this work, the melting point of pure silver nitrate has been taken as 208.6° C.

Experimental

Purity of Materials

The silver nitrate was obtained from British Drug Houses: it was 99.95% pure. It was recrystallized from aqueous solution and dried for several days over sulphuric acid.

The water used in all experiments was purified by distilling ordinary distilled water (*a*) from alkaline permanganate, (*b*) from baryta, and (*c*) through a block tin condenser.

Determination of the Ice Curve

This curve was determined by a well known technique, described, for instance, in the "Laboratory Manual of Physical Chemistry" of Davison, van Klooster, and Bauer (5, p. 56). The advantage of this method over the Beckmann method is that the equilibrium liquid phase is analysed; this

renders the measurements independent of supercooling. A Beckmann thermometer, calibrated against a standard thermometer and capable of being read to 0.005°, was used. The cooling bath was a tank of kerosene kept at −15° by a refrigerator unit.

Method of Analysis

All solutions were analysed with a precision within ±0.05% by well known electrolytic technique, the silver being deposited from double cyanide.

Thermostatic Control

In the temperature range −7° to 4° C. a thermostatically controlled, refrigerated kerosene-bath maintained temperatures to within ±0.18°.

For the range 4° to 20° C., an automatic refrigerator unit in conjunction with a small load heater in a water-bath permitted control to within ±0.04°.

Over the range 20° to 85° C., temperature was controlled to within ±0.04°, and to within ±0.07° from 85° to 145°.

All thermometers were mercury-in-glass, calibrated against certified standards. The Beckmann mentioned previously was used for temperatures from −7° to 0° C., and thermometers graduated in 0.1° and 0.2°, for temperatures from 0° to 100° and from 100° to 145°, respectively.

The Solubility Curve—Range −7° to 115° C.

The solubility curve was obtained by analysing solutions saturated at 5° C. intervals in the above range. A special apparatus, consisting of two glass vessels of capacities 150 cc. and 125 cc. respectively, was devised. These vessels were connected by ground glass joints. A mixture of silver nitrate and water was made up, such that at the temperature of investigation about five grams of solid phase would be present after the solution had become saturated. This mixture was placed in the larger vessel and suspended in the thermostat. The contents was stirred for a number of hours, by means of a glass stirrer passing through a mercury seal. The time of stirring varied greatly, the actual period depending on the temperature of the experiment. For temperatures from −7° to 55°, the solution was stirred overnight. For temperatures above 55°, the time of stirring was gradually shortened until at 85° it was only two hours. If the solution was stirred too long at the higher temperatures, metallic silver plated out on the stirrer. This result of hydrolysis indicates the presence of free nitric acid, which would influence the solubility. After saturation had been attained, the larger vessel was connected to the smaller (the receiver), and the entire apparatus was immersed in the thermostat. The saturated solution was then separated from the solid phase by applying reduced pressure to the exit tube. The saturated solution passed through a sintered glass filter into the receiver. The receiver was then stoppered, weighed, and the contents analysed. Above 75°, the suction produced sufficient evaporation of water, despite the rapidity of the operation, to cause some crystallization of silver nitrate in the receiver. Accordingly, above 75°, the desired filtration was brought about by applying compressed air to the orifice of the saturator. Even this method, however, became unsatis-

factory above 115°, because spontaneous evaporation is sufficiently rapid at these temperatures to cause crystallization in the receiver. At 115°, about nine parts of silver nitrate dissolve in one of water, so that the loss of even a few milligrams of water would cause considerable error.

Solubilities in the Range 115° to 145°

For this range, a pressure bomb was used. The bomb was made from steam boiler tubing. Its internal height was 20.0 cm. and internal diameter, 4.4 cm. It contained a glass vessel (the saturator) fitting tightly against the sides. The cover of the bomb was fitted with a gas tight stopcock, which was connected internally to a pipette and sintered glass filter. The bomb was rocked in a cradle in the thermostat by means of a motor and reducing gear. To carry out a determination with this apparatus, water and silver nitrate in appropriate proportions were placed in the saturator and liquefied by heating. The top of the bomb was then screwed on, whereby the pipette and attached filter were caused to dip into the solution. After equilibrium had been attained, filtration was brought about simply by opening the stopcock with the bomb still in the thermostat but with the stopcock projecting. The difference in vapour pressure drove the solution up through the filter into the pipette and eventually out of the cock. Above 145° C., the bomb method also became useless. At 145°, the saturated solution contains only about 5% of water, and the loss of the slightest trace of water vapour causes a considerable error.

Solubilities in the Range 145° to 194.9°

Since above 145° determinations of solubility as such are virtually impossible, the method of thermal analysis was used, i.e. instead of determining the concentration at fixed temperature, the temperature at which a fixed concentration separates crystals was determined. There is a considerable loss of accuracy in doing this, because, in this region of the curve, a comparatively large change of temperature causes only a slight change in solubility. Weighed quantities of silver nitrate and water were sealed into a thick-walled Pyrex tube, 2 cm. in diameter and 15 cm. long, fitted with a thermocouple well. The tube and contents were heated in a small electric furnace, temperatures being measured with an accuracy of $\pm 0.1°$ with an iron–constantan thermocouple that had been calibrated against the freezing points of pure lead and pure tin and the boiling point of water. Plato's method of graduated cooling (14) was employed, the temperature being reduced at a uniform rate of 0.5° per min. by suitable adjustment of a rheostat in series with the furnace.

Results

In Tables I and II all concentration values are expressed as grams of silver nitrate per 100 gm. of solution.

The eutectic point was found experimentally to be at $-7.57°$ C. and a concentration of 46.9% of silver nitrate. This was checked by direct observation that a mixture of this composition, made by direct weighing, showed a

TABLE I

THE ICE CURVE FOR THE SYSTEM: SILVER-NITRATE–WATER

Temp., °C.	−1.89	−3.55	−5.00	−6.36	−7.22
Conc.	10.41	19.72	30.04	39.16	44.72

TABLE II

SOLUBILITY OF SILVER NITRATE IN WATER

Temp., °C.	Conc.	Temp., °C.	Conc.	Temp., °C.	Conc.	Temp., °C.	Conc.
(a) Range −7 to 115° C.: estimated error, ±0.05%							
−6.51	48.13	25.18	70.96	55.29	80.24	95.43	87.59
−0.88	54.04	30.57	72.81	59.99	81.49	103.57	88.44
4.32	58.64	35.48	74.31	64.92	82.98	114.25	89.74
10.41	63.11	40.07	75.80	70.61	83.92		
15.37	65.90	44.98	77.47	76.02	84.03		
19.66	68.20	50.16	78.95	84.42	86.17		
(b) Range 115 to 145° C. (bomb apparatus): estimated error, ±0.5%							
124.05	90.42	134.65	92.23	146.10	93.52		
(c) Range 145 to 195° C. (thermal analysis): estimated error, ±0.5%							
142.0	93.05	155.0	95.45	168.0	97.02	194.9	99.06
151.1	94.49	160.9	96.45	181.1	98.07		

constant temperature of crystallization of −7.6°. The results obtained here are to be compared with the values −7.3° and 47.1%, recorded by Middelberg (13) and Schreinemakers (18).

Discussion of Results

Of the previous investigations of the ice curve, the work of Raoult (15) is the most important in relation to that of the writers. Our results agree well with his, the maximum deviation being +0.13° at a concentration of 22.91% of silver nitrate and temperature of −3.97° C. It was to be expected that our solubility figures would not agree with those of other workers, since theirs are not consistent with themselves. The greatest deviations are:— +3.0% (Etard, 5°) and −3.2% (Tilden and Shenstone, 125°).

The general form of the equilibrium curve is well known (7): there is no object in reproducing it here, since our data are more accurate than any that can be represented on a curve of reasonable size. A small section of the

curve, however, is plotted in Fig. 1, to show the break that occurs in the solubility curve at 159° C.: at this temperature, silver nitrate passes from the rhombic to the rhombohedral form. This is not claimed as a new determination of the transition point (it has been determined more accurately by others) but rather as a verification of theory. The relative curvature in this

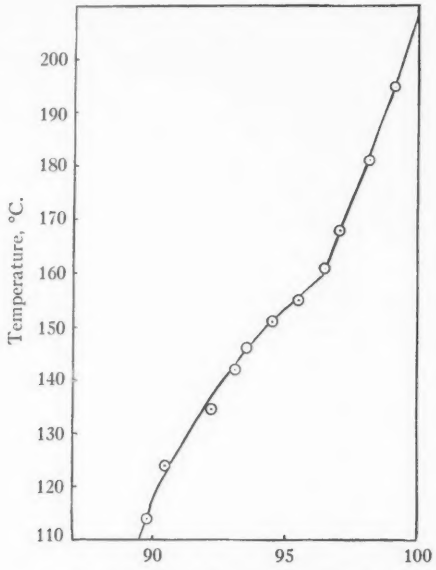

FIG. 1. *Temperature–concentration diagram of the system: silver-nitrate–water, between 110° and 220°, under the vapour pressure of the system.*

region also agrees with theoretical prediction. Theory requires that a point on the metastable prolongation must be richer in silver nitrate than the corresponding point on the stable curve, and this is seen to be so. We admit that this discontinuity would probably have been overlooked if we had not been aware that such a transformation exists. Nevertheless, the figures admit the showing of such a discontinuity, without violence.

References

1. ARRHENIUS, S. Z. physik. Chem. 2 : 491-505. 1888.
2. BAILEY, C. R. J. Chem. Soc. 1534-1539. 1930.
3. BENRATH, A., GJEDEBO, F., SCHIFFERS, B., and WUNDERLICH, H. Z. anorg. allgem. Chem. 231 : 285-297. 1937.
4. BRIDGMAN, P. W. Proc. Am. Acad. Arts Sci. 51 : 581-625. 1916.
5. DAVISON, A. W., VAN KLOOSTER, H. S., and BAUER, W. H. Laboratory manual of physical chemistry. 3rd ed. J. Wiley and Sons, Inc., New York. 1941.
6. ETARD, M. Ann. chim. phys. (Sér. 7) 2 : 503-574. 1894.

7. FINDLAY, A. and CAMPBELL, A. N. The phase rule and its applications. 8th ed. rev. Longmans, Green, and Company, London. 1938.
8. GUINCHANT, M. Compt. rend. 149 : 569-571. 1909.
9. GUTHRIE, F. Phil. Mag. (Ser. 5) 1 : 354-369. 1876.
10. HISSINK, D. J. Z. physik. Chem. 32 : 537-563. 1900.
11. JÄNECKE, E. Z. physik. Chem. 90 : 280-295. 1915.
12. KREMERS, P. Ann. Physik, 92 : 497-520. 1854.
13. MIDDELBERG, W. Z. physik. Chem. 43 : 305-353. 1903.
14. PLATO, W. Z. physik. Chem. 55 : 721-737. 1906.
15. RAOULT, F. M. Z. physik. Chem. 2 : 488-490. 1888.
16. ROTH, W. A. Z. physik. Chem. 79 : 599-620. 1912.
17. RÜDORFF, F. Ann. Physik, 145 : 579-622. 1872.
18. SCHREINEMAKERS, F. A. H. Z. physik. Chem. 65 : 553-585. 1909.
19. SCHREINEMAKERS, F. A. H. and DE BAAT, W. C. Chem. Weekblad, 7 : 259-264. 1910.
20. SCHWARZ. Zur Kenntnis der umkehrbaren Umwandlungen polymorpher Körper. Göttingen. 1897.
21. TILDEN, W. A. and SHENSTONE, W. A. Trans. Roy. Soc. (London) A, 175 : 23-36. 1884.
22. VAN EYK, C. Z. physik. Chem. 51 : 721-731. 1905.
23. ZAWIDZKI, J. VON. Z. physik. Chem. 47 : 721-728. 1904.

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